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(54) A method of making and applying beta-limit dextrin containing starch hydrolysates.

EP 0 242 913 A2 (57) A method of making beta-limit dextrin containing starch products is disclosed. The method comprises first treating fully or partially gelatinized starch with beta-amylase until a DE of 5-30 is reached, thereafter completely gelatinizing the resulting product as far as necessary and treating the resulting solution with alpha-amylase for a short period of time so that, as a result of the treatment with alpha-amylase, the DE of the starch hydrolysate is increased by no more than 3 units.

## A method of making and applying beta-limit dextrin containing starch hydrolysates

This invention relates to a method of making and applying beta-limit dextrin containing starch products, and to the application of the products made in foods and pharmaceuticals.

In the depolymerization of dissolved starch with beta-amylase, 1,4-glucosidic bonds are broken from the non-reducing terminal groups of the starch molecules, whereby maltose is split off. When a branch point (1,6-glucosidic bond) or a modified glucose unit (e.g. phosphorylated or oxidized) is approached, the hydrolysis by the beta-amylase is terminated. In the case of amylopectin, this will commonly be the case at a 1,6-glucosidic bond (branch point), leaving an amylopectin molecule virtually stripped of its side chains. Such molecules and their products of hydrolysis with an average degree of polymerization in excess of 100 are referred to hereinafter as beta-limit dextrin. Amylose consists of unbranched and/or little branched chains and, in molecular dissolved form, is converted virtually completely into maltose by beta-amylase. Owing to the action of beta-amylase on starch, there is thus obtained a starch hydrolysate which consists as to 40-80% by weight of beta-limit dextrin and as to 20-60% by weight of maltose.

As early as 1814 Kirchhoff described a process in which gelatinized potato starch was treated with malt (contains beta-amylase). The result was a mixture of maltose and beta-limit dextrin. Thereafter, corresponding methods have been described in many publications. Up to now, however, substantial industrial production of beta-limit dextrin containing starch hydrolysates has not come about.

It is an object of the present invention to provide an improved process for the manufacture of beta-limit dextrin containing starch hydrolysates. It is another object of the present invention to provide a process for the use of beta-limit dextrin containing starch hydrolysates in foods and pharmaceuticals.

The method according to the invention is characterized by treating fully or partially gelatinized starch first with a purified beta-amylase until a DE (dextrose-equivalent) of 10-30 is reached, whereafter the resulting product, as far as necessary, is completely gelatinized and the solution treated for a short time with alpha-amylase so that owing to the treatment with alpha-amylase, the DE of the starch hydrolysate is increased by no more than 3 DE units.

There are considerable differences in composition and properties between the various commercial starches. This has been described by J.J.M. Swinkels in *Starch/Stärke*, 37 (1985), Nr.1, pp. 1-5.

In principle, all starches can be used for the method according to the present invention. The most suitable starches, however, are potato starch, tapioca starch and the waxy starches (for example, waxy corn starch).

Before the action of beta-amylase on the starch molecules, the starch granules must first be fully or partially gelatinized. In one embodiment of the invention, an aqueous starch suspension is heated until the viscosity is increased from initial gelatinization. The beta-amylase is caused to act on the suspension of swollen starch granules under such conditions (time, temperature) that the granular form of the starch is largely maintained. During the hydrolysis, a portion of the starch molecules (in particular the amylose molecules) are dissolved from the swollen granules and are there decomposed by the beta-amylase to, in the main, maltose. In another embodiment of the method according to the invention, the starch is first fully gelatinized in water, whereby the granular structure is totally lost. This can be effected, for example, by means of a steam injection apparatus (jet cooker) at 100-200°C. After cooling the resulting starch solution to, for example, 80-50°C, beta-amylase is added.

The starch concentration before the hydrolysis with beta-amylase is preferably 10-40% by weight. The beta-amylase compositions used must be purified so that, in particular, there is substantial absence of alpha-amylase activity and glucoamylase activity. Examples of suitable compositions are beta-amylase compositions isolated from soya and beta-amylase compositions isolated from certain bacteria. The beta-amylase is caused to act on the starch at a temperature of preferably 55-70°C. Hydrolysis is continued until a DE of 5-30, and preferably of 10-25, is reached. If necessary (in case the hydrolysis was carried out with swollen granules), after the hydrolysis with beta-amylase, the starch granules are completely gelatinized by means, for example, of a jet cooker. Instead of beta-amylase, other exo-amylases can be used, such as glycoamylase and phosphorylase, and those isolated from the bacteria *Pseudomonas stutzeri* and *Aerobacter aerogenes*.

The starch hydrolysate solution obtained after the treatment with beta-amylase is subsequently treated with an alpha-amylase composition for a short time. As a result, the viscosity of the solution is considerably decreased. Preferably, the duration of the treatment is about 1-15. The degree of action on the alpha-amylase is determinative of the degree of polymerization of the resulting beta-limit dextrin. The treatment with alpha-amylase is car-

ried out in such a manner that, as a result of the action of the alpha-amylase, the DE value of the hydrolysate is increased by no more than 3 DE units, and preferably by no more than 2 DE units. Subsequently, the hydrolysis of alpha-amylase is stopped by deactivating the enzyme (by reducing the pH or heating).

After stopping the alpha-amylase, the resulting solution can be converted, for example, by spray drying, into a dried starch hydrolysate with a DE of, for example, 5-30, which can be used as such.

In another embodiment of the method according to the invention, after stopping the alpha-amylase, beta-amylase is again added to the hydrolysate. Owing to the action of the beta-amylase, the maltose content rises further, as a result of which the DE of the hydrolysate is increased to, for example, DE 30-45. In this second action period, too, we preferably use purified beta-amylase at a temperature of 55-70°C. The hydrolysate then obtained can be purified, for example, by filtration. The resulting solution can be converted, for example, by spray drying, into a dried starch hydrolysate consisting as to 30-50% by weight of beta-limit dextrin and as to 50-70% by weight of maltose. Owing to the presence of the high molecular beta-limit dextrans, spray drying can be satisfactorily accomplished in spite of the presence of a high maltose concentration. It is also possible, however, to convert the resulting solution into one product consisting substantially of beta-limit dextrin and another product consisting virtually exclusively of maltose, by means of ultrafiltration, activated carbon, ion exchangers, organic solvents, or dialysis.

In a further embodiment of the method according to the invention, after stopping the alpha-amylase, a precipitate is caused to form in the solution, which for the most part (more than 50% by weight) consists of amylose. The formation of the precipitate is promoted by decreasing the temperature of the solution. The precipitate can be separated from the solution, for example, by filtration, decanting, or centrifugation. The resulting amylose-rich material is suitable as a filler and binder in tablets, and as a gelatin substitute in confections and capsules. The amylose material can also be used in packaging materials (amylose film) as a coating on fruit, foods and pharmaceuticals, in noodles and other doughs, as a sizing agent for glass fibers and other fibers, as a complexing agent for various substances, and as a gelating agent in foods, pharmaceuticals and cosmetics. Furthermore, the resulting amylose-rich material is suitable as a component in tablets, capsules and the like for the sustained release of active materials. The remaining liquid phase is a solution of beta-limit dextrin and maltose and can

be dried as such. It is also possible, however, by ultrafiltration etc. to isolate the individual components, i.e. beta-limit dextrin and maltose, from the solution.

The mixture of beta-limit dextrin and maltose described hereinbefore and the beta-limit dextrin fraction isolated therefrom can be used in various foods and pharmaceutical products. Examples are confections with a gum structure (gums, liquorice and the like), extruded confections, soft drinks (stabilizer), bakery products (cake and the like), viscous dairy products (puddings and custards), coatings, deep-freeze products and tablets. Beta-limit dextrans can also be used as a carrier of dried liquids, such as fruit juices, soups, sauces, milk beverages, etc. When used in confections, the mixture of beta-limit dextrin with maltose functions both as a binder (beta-limit dextrin) and as a sweetener (maltose).

The invention is illustrated in and by the following examples.

#### Example 1

To a suspension of potato starch in water (20% by weight of solids) 0.3% (by weight, calculated on solids content) of a beta-amylase composition, isolated from soya and purified was added. Subsequently the stirred suspension was heated to 60°C. Thereafter the suspension was slowly warmed up to 65°C during 4 hours. During this period, the granular form was retained and the DE of the mixture increased to 18. Subsequently the suspension was pumped to a jet cooker, in which the suspension was gelatinized with steam at 140°C. After cooling to 80°C 0.1% (by weight, calculated on dry matter) of an alpha-amylase composition (isolated from *Bacillus subtilis*) was added to the solution. After an alpha-amylase period of 5 minutes, the reaction was stopped by decreasing the pH to 2.5. The DE was then 19. Subsequently the hydrolysate was neutralized with soda to a pH of 4.8. Thereafter, 0.1% (by weight, calculated on dry matter) of the above beta-amylase composition was added, which was allowed to act at 65°C for 3 hours. Thereby a DE of 40 was obtained. Finally, the hydrolysate was filtered and spray dried. The resulting product consisted of a mixture of 44% by weight (calculated on the dry matter) of beta-limit dextrin, 44.5% by weight of maltose and 1.5% by weight of maltotriose.

### Example 2

A potato starch suspension (20% by weight of dry matter; pH 6.0) was gelatinized in a jet cooker at 155°C. After cooling to 65°C, 0.1% (by weight, calculated on dry matter) of a beta-amylase composition, isolated from soya was added to the starch solution. The beta-amylase was allowed to act at 65°C for 2 hours, whereby a DE of 23 was attained. Subsequently, the hydrolysate was heated to 100°C, whereafter 0.05% (by weight, calculated on dry matter) of an alpha-amylase composition (isolated from *Bacillus licheniformis*) was added. After an action period of 3 minutes, the alpha-amylase was deactivated by decreasing the pH to 2.5. The DE of the hydrolysate was then 24. Subsequently, the pH was adjusted to 4.8 with soda, whereafter 0.1% (by weight, calculated on dry matter) of the above beta-amylase composition was added. The beta-amylase was allowed to act for 3 hours at 63°C, whereby a DE of 32 was reached. Finally, the solution was filtered and spray dried. The dried starch hydrolysate contained 49% by weight (calculated on dry matter) of beta-limit dextrin, 50% by weight of maltose and 1% by weight of maltotriose.

### Example 3

A suspension of waxy corn starch in water (23 parts by weight of dry matter; pH 6.7) was heated in a jet cooker to 160°C. After cooling to 65°C and pH adjustment to 5.8, 0.075% (by weight, calculated on starch solids) of a beta-amylase composition isolated from soya was added to the resulting starch solution. After a reaction period of 2 hours, the DE was 20. The beta-amylase was then deactivated by reducing the pH to 2.7. After pH adjustment to 4.8, 0.004% (by weight, calculated on starch solids) of alpha-amylase (Optiamyl L 480) was added at 50°C. After 30 minutes, the DE was 22, and the alpha-amylase was stopped by adjusting the pH to 2.7. After separation of the insolubles, a clear stable solution was formed. Calculated on the solids content, the end product contained 34% of maltose and 66% of beta-limit dextrin, by weight.

### Example 4

A potato starch suspension (22% by weight of solids; pH 5.5) was converted into a starch solution by means of a jet cooker at 160°C. After cooling to 70°C, 0.1% (by weight, calculated on dry matter) of a beta-amylase composition isolated from soya was added. The beta-amylase was allowed to react

at 65°C for 1.5 hours, whereby a DE of 17 was reached. After deactivating the beta-amylase and cooling to 50°C, 0.05% (by weight, calculated on solids) of alpha-amylase was allowed to act on the mass for 10 minutes, whereby a DE of 18 was reached. Subsequently, the alpha-amylase was deactivated by reducing the pH to 2.5. Thereafter, the hydrolysate was allowed to stand at 40°C for 18 hours. A precipitate was formed, which consisted as to 89% by weight of amylose. By filtration, the amylose precipitate was separated from the solution. The dried precipitate contained 20% of the weight of the starting material in potato starch (on solids basis). The filtrate was clear and consisted as to 50% by weight (calculated on dry matter and on the potato starch) of beta-limit dextrin and as to 30% by weight (calculated on the dry matter and on the potato starch) of maltose. By ultrafiltration the filtrate was split into one fraction rich in beta-limit dextrin and another fraction rich in maltose.

### Example 5

This example illustrates the use of the spray dried product obtained according to Example 1 as a combined binder (beta-limit dextrin component) and sweetener (maltose component) in the manufacture of gum-like confections (clear gums).

In a steam-heated kettle with a high-rate stirrer, 70.5 parts by weight of the spray dried mixture of beta-limit dextrin and maltose (obtained in accordance with Example 1) and 28.5 parts by weight of water were homogeneously mixed at a temperature of 70-80°C. The mixed product was then passed to a jet cooker at 130°C. Thereafter 1 part by weight of citric acid and also colours and flavours were added to the resulting solution. Subsequently the solution was cast into moulds at 70°C and dried at 60°C for 24 hours. The end products had a good gum-like structure (as regards elasticity and chewability) and the desired clarity.

### Example 6

A mixture was made of 83.3 parts by weight of the combination of beta-limit dextrin and maltose (obtained according to Example 2); 1 part by weight of sal-ammoniac; 0.06 part by weight of aniseed oil; 0.48 part by weight of caramel; 0.13 part by weight of glycerolmonostearate and 7.3 parts by weight of water. This mixture was continuously supplied to an extruder and extruded at 75-100°C (Brabender extruder). After cooling, an elastic liquorice product of good gum structure was obtained.

## Claims

1. A method of making beta-limit dextrin containing starch products, characterized by first treating fully or partially gelatinized starch with beta-amylase until a DE of 5-30 is reached, whereafter the resulting product, as far as necessary, is completely gelatinized and the resulting solution is treated for a short period of time with alpha-amylase so that, as a result of the treatment with alpha-amylase, the DE of the starch hydrolysate is increased by no more than 3 units.

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2. A method as claimed in claim 1, characterized in that beta-amylase is caused to act on a starch suspension of swollen starch granules.

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3. A method as claimed in claim 1, characterized in that beta-amylase is caused to act on a starch solution in which the starch has lost the granular form.

4. A method as claimed in claim 1, characterized by drying the hydrolysate after the action of the alpha-amylase.

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5. A method as claimed in claim 1, characterized in that, after the hydrolysis with alpha-amylase, beta-amylase is again allowed to act on the hydrolysate until a DE of 25 to 45 is reached.

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6. A method as claimed in claim 1, characterized in that, after the hydrolysis with alpha-amylase, an amylose-rich precipitate is caused to form in the resulting solution, and the resulting precipitate is subsequently separated.

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7. A method as claimed in claims 1-6, characterized by drying the resulting solution of beta-limit dextrin and maltose.

8. A method of making gum-like confections, characterized by using therein a beta-limit dextrin containing starch product produced in accordance with any of claims 1-7.

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9. Gum-like confections made by the method as claimed in claim 8.

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(54) A method of making and applying beta-limit dextrin containing starch hydrolysates.

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# EUROPEAN SEARCH REPORT

Application Number

EP 87 20 0685

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	CEREAL CHEMISTRY, vol. 59, no. 6, 1982, pages 488-492, American Association of Cereal Chemists, Inc.; J.E. KRUGER et al.: "High-performance aqueous gel permeation chromatographic analysis of beta-limit dextrin hydrolysis by malted hard red spring wheat, malted durum wheat, and fungal ( <i>Aspergillus oryzae</i> ). alpha-amylases" * Page 489-490 *	1-6	C 12 P 19/22 C 12 P 19/14 A 23 G 3/00
Y	J. BIOCHEM., vol. 78, no. 5, 1975, pages 897-903; K. UMEKI et al.: "Structures of multi-branched dextrans produced by saccharifying alpha-amylase from starch" * Page 898, right-hand column *	1-6	
X	PATENT ABSTRACTS OF JAPAN, vol. 62, no. 44, 2nd December 1982, page 123 C 138; & JP-A-57 144 948 (NIKKEN KAGAKU K.K.) 07-09-1982 * Whole abstract *	1-9	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
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A	CHEMICAL ABSTRACTS, vol. 97, 1982, page 527, no. 71158w, Columbus, Ohio, US; & JP-A-82 74 057 (NIKKEN CHEMICALS CO., LTD) 10-05-1982 * Whole abstract *		
-/-			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-06-1988	Examiner LENSEN H.W.M.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document	



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 005 867 (MILLIPORE CORP.) ---		
A	DE-A-2 227 976 (A. PURR) ---		
A	US-A-2 266 051 (H. LEBESON) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-06-1988	Examiner LENSSEN H.W.M.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	